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④ Thermally resistant butadiene polymer composition.

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Description

The present invention relates to a butadiene polymer composition having thermal resistance.

Butadiene polymers such as solution-polymerized polybutadiene rubber (BR), solution-polymerized 5 styrene-butadiene copolymeric rubber (SBR), styrene-butadiene block copolymers (SBS), etc. are generally produced by anionic polymerisation in a hydrocarbon solvent using a Ziegler catalyst or organo-lithium compound catalyst. However, these butadiene polymers have the defect that they are inferior in thermal resistance; for example, SBS generates fish-eye gel because of its poor thermal resistance under the higher processing temperatures and rates required for film extrusion, causing problems such as marked 10 reduction in the physical properties of the film.

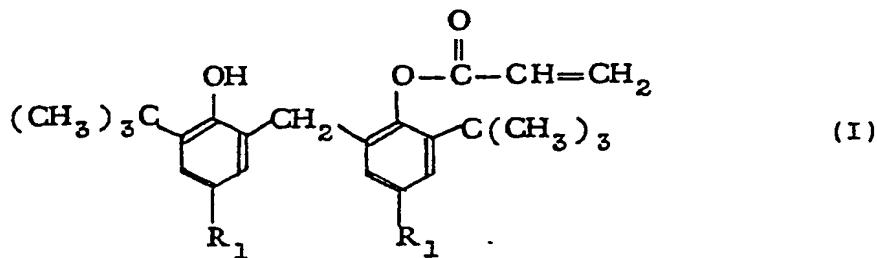
Also, in the conventional production of BR, SBR, etc., the steam stripping method is employed to remove the polymerization solvent from the polymerization solution after completion of polymerization. In recent years, however, the solvent-direct-drying method, which in theory can minimise the quantity of steam used, has been proposed because of energy saving; in this method, however, the reaction solution 15 after polymerization is generally treated at a temperature above 150°C, which is considerably higher than the boiling point of the polymerization solvent, and this causes new problems such as gel formation during the treatment, etc. Thus, an improvement in the thermal resistance of butadiene polymers, particularly in the absence of oxygen, has been needed.

It is well known that, in order to stabilize such butadiene polymers, various kinds of phenolic, 20 phosphorus-containing and sulfur-containing antioxidants can be added in the course of production and processing of the polymers. For example, there are well known the use of phenolic antioxidant alone such as 2,6-di-tert-butyl-4-methylphenol, 2,2'-methylenebis(4-methyl-6-tert-butylphenol), n-oc-tadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, triethylene glycol bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate], pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, etc.; and the use of above phenolic antioxidant in combination with phosphorus-containing antioxidant such as tris-(nonylphenyl)phosphite, distearyl pentaerythritol diphosphite, etc., or with sulfur-containing antioxidant such as dilauryl thiodipropionate, dimyristyl thiodipropionate, distearyl thiodipropionate, pentaerythritol tetrakis(3-laurylthiopropionate), etc.

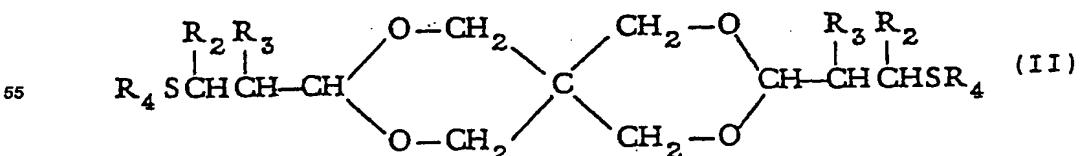
These methods prevent gel formation caused by oxidative degradation, but do not satisfactorily prevent gel formation caused by heat in the absence of oxygen.

We have found that butadiene polymer composition which is very stable to gel formation by heat in the absence of oxygen is obtained by incorporating, in a particular ratio range, phenolic compound having a particular structure with sulfur-containing compound having a particular structure.

35 The present invention provides a butadiene polymer composition containing at least one phenolic compound (I)



wherein the R1's are the same or different C1-C4 alkyl groups and at least one sulfur-containing 50 compound (II)

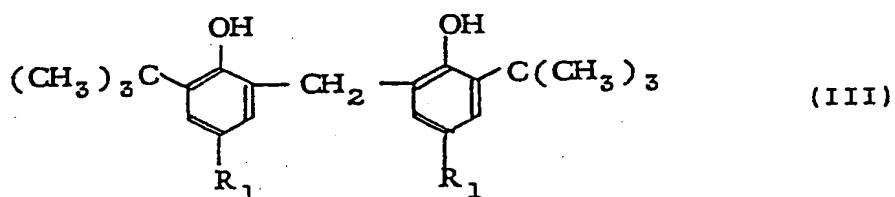


wherein the R_2 's and R_3 's are selected independently from a hydrogen atom and $C_1 - C_6$ alkyl groups and the R_4 's are the same or different $C_3 - C_{18}$ alkyl groups, the weight ratio of formula (I) compound to formula (II) compound being 1:0.5 to 1:10 and the total amount of compounds (I) and (II) being 0.1 to 3 parts by weight based on 100 parts by weight of butadiene polymer.

5 In the phenolic compounds of formula (I), a substituent R_1 is preferably a methyl or ethyl group, particularly preferably a methyl group, for performance as a thermal degradation inhibitor.

Such phenolic compounds can be produced by reacting 2,2'-methylenebis(6-tert-butyl-4-alkyl-phenol) of general formula (III)

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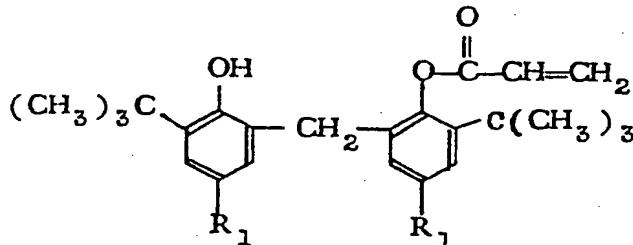
(wherein the R_1 's are as above) with acrylic acid or its lower alkyl ester or acid chloride by the well-known method.

20 Representative examples of such phenolic compounds are shown in Table 1.

TABLE 1

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Abbrevia- tion	R_1
I - 1	$-CH_3$
I - 2	$-CH_2CH_3$
I - 3	CH_3 $-CHCH_2CH_3$
I - 4	$-C(CH_3)_3$

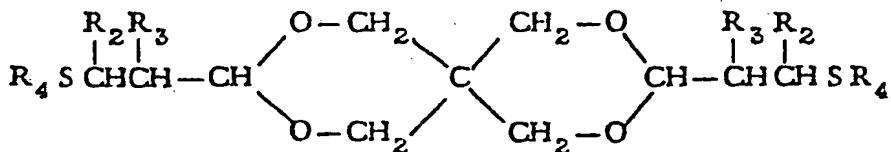
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In the sulfur-containing compounds of formula (II), substituents R_2 and R_3 are preferably a hydrogen atom or $C_1 - C_3$ alkyl groups for thermal and oxidation stability, and substituents R_4 are preferably $C_{12} - C_{18}$ alkyl groups for the same reason.

Representative examples of such sulfur-containing compounds are shown in Table 2.

TABLE 2



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Compound No.	R ₂	R ₃	R ₄	
20	II - 1	-CH ₃	-H	-C ₈ H ₁₇
25	II - 2	-C ₄ H ₉	-H	-C ₁₂ H ₂₅
30	II - 3	-CH ₃	-H	-C ₁₂ H ₂₅
35	II - 4	-H	-H	-C ₁₂ H ₂₅
	II - 5	-CH ₃	-H	-C ₁₈ H ₃₇
	II - 6	-H	-CH ₃	-C ₁₈ H ₃₇

Such sulfur-containing compounds can be produced by reacting pentaerythritol with aldehyde(s) represented by the general formula



45 (wherein the R₂, R₃ and R₄ moieties are as defined above) according to the conventional acetalization procedure.

The total amount of compounds (I) and (II) incorporated is preferably 0.2 to 2 parts by weight, based on 50 100 parts by weight of butadiene polymer.

The proportion of compound (I) to compound (II) is preferably from 1:1 to 1:5 by weight.

For incorporating compounds (I) and (II) in butadiene polymer, conventional methods (for example adding the compounds to the polymerization solution after completion of anionic polymerization, or directly adding them during the extrusion - granulation or molding step, etc.) can be employed.

55 The butadiene polymer composition of the present invention may contain other additives as need arises, and such additives include for example ultraviolet absorbers, light stabilizers, antioxidants, metal inactivators, metal soaps, nucleating agents, lubricants, antistatic agents, flame retardants, pigments, fillers, etc.

Particularly, the weather resistance of the composition can be improved by incorporating ultraviolet absorbers, hindered amine light stabilizers, etc. such as 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-n-octoxybenzophenone, 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-(2-hydroxy-3-tert-butyl-5-methylphenyl-5)-chlorobenzotriazole, 2-(2-hydroxy-3,5-di-tert-butylphenyl)-5-chlorobenzotriazole, 2-(2-hydroxy-3,5-di-tert-butylphenyl)benzotriazole, 2,4-di-tert-butylphenyl 3',5'-di-tert-butyl-4'-hydroxybenzoate, (2,2'-thiobis(4-tert-octylphenolate))butylamine Ni salt, 2,2,6,6-tetramethyl-4-piperidinyl benzoate, bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) 2-[3,5-di-tert-butyl-4-hydroxybenzyl]-2-n-butylmalonate, 1-[2-{3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy}ethyl]-4-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-2,2,6,6-tetramethylpiperidine, dimethyl succinate, 1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine polycondensation products, poly{[6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidyl)imino]-hexamethylene[-(2,2,6,6-tetramethyl-4-piperidyl)imino]}, poly{[6-morpholino-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidyl)imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino]}, etc.

Also, the color of the composition can be improved by incorporating phosphite antioxidants such as distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl)phosphite, tris(2-tert-butyl-4-methylphenyl)phosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, tetrakis[2,4-di-tert-butylphenyl]-4,4'-biphenylene diphosphite, etc.

Butadiene polymers for use in the present invention include solution-polymerized polybutadiene rubber (BR), solution-polymerized styrene-butadiene copolymeric rubber (SBR), styrene-butadiene block copolymers (SBS), impact-resistant polystyrene modified with BR, SBR or SBS (HI-PS), acrylonitrile-butadiene-styrene copolymers (ABS), etc. These butadiene polymers may be used alone or in mixture with other polymers.

The present invention is illustrated by the following reference examples and examples, but is not limited thereto.

Reference example 1 Synthesis of the compound I-1

To a 200-ml four-necked flask equipped with a thermometer, a stirrer, a condenser and a dropping funnel were added 17.03 g (0.05 mole) of 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 3.60 g (0.05 mole) of acrylic acid, 11.13 g (0.11 mole) of triethylamine and 70 g of toluene, and after replacing the air in the flask by nitrogen, 12.27 g (0.08 mole) of phosphorus oxychloride was added dropwise over 20 minutes with stirring. After completion of the addition, stirring was continued at room temperature for 1 hour. After completion of the reaction, the organic layer was washed with water, and toluene in the organic layer was removed by distillation under reduced pressure. The residue obtained was recrystallized from n-hexane to obtain 16.77 g of the desired compound having a melting point of 133 to 134°C as white crystals (yield, 85%).

Reference example 2 Synthesis of the compound II-4

To a 100-ml flask equipped with a drain pipe were added 2.58 g (0.01 mole) of 2-dodecyl-thiopropionaldehyde, 0.68 g (0.005 mole) of pentaerythritol, 0.095 g (0.0005 mole) of p-toluenesulfonic acid monohydrate and 50 ml of toluene, and the mixture was refluxed for 8 hours at a temperature of 110°C while removing water. After completion of the reaction, the reaction mixture was cooled, neutralized with sodium methylate, washed with eight 200-ml portions of water and separated into aqueous and oily layers. The oily layer was concentrated by distillation, and the residue obtained was washed with isopropanol to obtain 2.5 g of the desired compound having a melting point of 64 to 65°C as white crystals.

Example 1

In a nitrogen gas atmosphere, 0.08 part by weight of n-butyl lithium was added to a cyclohexane solution containing 15 parts by weight of 1,3-butadiene. After polymerization was carried out for 1 hour at a temperature of 70°C, 20 parts by weight of styrene, 15 parts by weight of 1,3-butadiene and 50 parts by weight of styrene were added in this order, and polymerization was carried out for 1 hour at a temperature of 70°C for each addition of the compounds. After completion of the polymerizations, required amounts of the test compounds shown in Table 1 were added, and cyclohexane was removed by heating in a nitrogen gas atmosphere to obtain a block copolymer of B-A-B-A structure having a butadiene content of 30 wt. %.

Using the block copolymer obtained, a thread-like extrusion test was carried out on a lab-plastomill extruder under the conditions described below, and the gel content of the thread-like extrudate obtained was measured as toluene-insoluble matter. The result is shown in Table 1.

The gel content was measured as follows: About 1 g of the thread-like test sample was accurately weighed and dipped in 200 ml of toluene; after stirring for 24 hours, the solution was filtered through a 200-mesh wire net, and the insoluble matter was dried and weighed; and the gel content was calculated from the weight ratio of the insoluble matter to the test sample.

Test conditions:

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- (1) Tester Lab-plastomill Type 40-100 (Toyo Seiki Co.)
 (2) Extruder Type D 20-25 (Toyo Seiki Co.)
 (3) Measurement conditions

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Strand die diameter	1 mmØ
Cylinder temperature	230-260 °C
Number of rotations	8 r.p.m.
Falling distance	93 cm

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Example 2

In a nitrogen gas atmosphere, 1,3-butadiene was polymerized at a temperature of from 60° to 65°C in n-hexane with n-butyl lithium as catalyst. After completion of the polymerization, required amounts of the test compounds shown in Table 2 were added, and n-hexane was removed by heating in a nitrogen gas atmosphere to obtain polybutadiene rubber (BR).

Using the polybutadiene rubber obtained, a kneading test was carried out in a nitrogen gas stream on a lab-plastomill (Type 40-100, a product of Toyo Seiki Co.), and gelation prevention on kneading was evaluated by torque behavior accompanying gelation. The result is shown in Table 2.

The gelation preventing effect is expressed by the time required for the torque to reach a peak (gelation time); a longer gelation time means a higher gelation preventing effect. Test condition on lab-plastomill:

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- (1) Mixer Type R-60
 (2) Range of measurable torque 0-500 kg·cm
 (3) Amount fed 30 g
 (4) N₂ flow rate 1 liter/min.
 (5) Test temperature 180 °C
 (6) Number of rotations 10 r.p.m. for 3 minutes for pre-heating; 60 r.p.m. after pre-heating.

The symbols AO-1 etc. in Tables 1 and 2 represent the following compounds.

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- AO-1: n-Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
 AO-2: 2,6-Di-tert-butyl-4-methylphenol
 AO-3: Pentaerythritol tetrakis(3-laurylthiopropionate)
 AO-4: Dimyristyl thiodipropionate

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Table 1 Amounts (FHRI) and test results

Test Compound No.	Example of invention												Comparative example			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14		
I - 1	0.2	0.2	0.2		0.2										0.2	
I - 2				0.2	0.2	0.2										
AO-1																
AO-2																0.2
II - 4	0.4	0.8	0.4												0.2	
II - 5			0.4		0.4										0.2	
AO-3																0.2
AO-4																0.2
GeI content (wL%)	0.0	0.0	0.0	0.1	0.1	0.7	1.0	1.5	8	35	37	36	40	0.4		

Table 1 Amounts (ml/l) and test results (Cont'd.)

Test compound No.	Comparative example					
	15	16	17	18	19	20
I - 1	0.2					
Phenolic compound	I - 2	0.2				
AO-1		0.2	0.2	0.2	0.2	No addition
AO-2			0.2	0.2	0.2	
Sulfur-containing compound	II - 4		0.4	0.4		
II - 5				0.4	0.4	
AO-3		0.4				
AO-4	0.4					
Gel content(wt.%)	0.6	0.6	1.1	5	10	480

Table 2 Amounts (mM) and test results

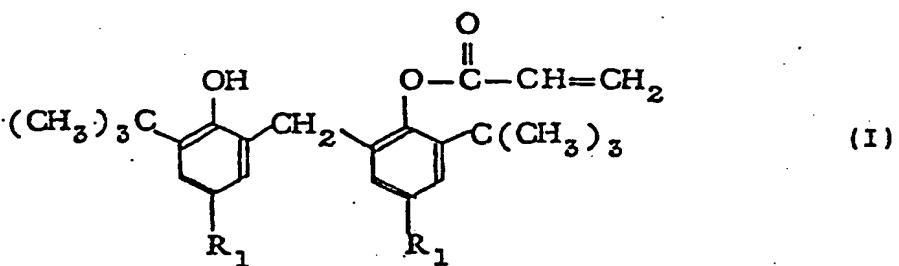
Test compound	Example of invention												Comparative example			
	No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
I - 1	0.2	0.2				0.2										0.2
I - 2			0.2	0.2			0.2									
AO-1								0.2								
AO-2									0.2							
II - 4	0.4	0.8		0.4					0.2							0.2
II - 5			0.4		0.4					0.2						
AO-3											0.2					0.4
AO-4												0.2				
Gelation time (minutes)	35	38	34	31	30	19	16	4	7	3	3	3	3	3	3	24

Table 2 Amounts (PHR) and test results (Cont'd.)

		Comparative example														
Test compound	Mn.	15	16	17	18	19	20	21	No addition	0.2	0.2	0.4	0.4	0.4	0.4	
		I - 1	I - 1	I - 2	I - 2	phenolic compound	AO-1	AO-2								

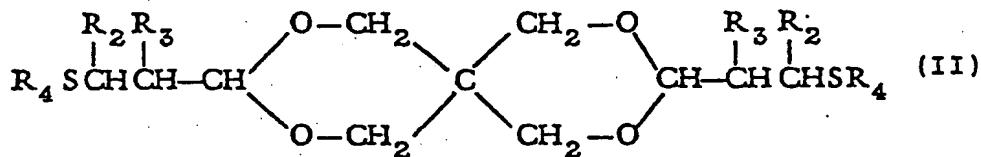
Claims

1. A butadiene polymer composition containing at least one phenolic compound (I)



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wherein the R₁'s are the same or different C₁ - C₄ alkyl groups and at least one sulfur-containing compound (II)

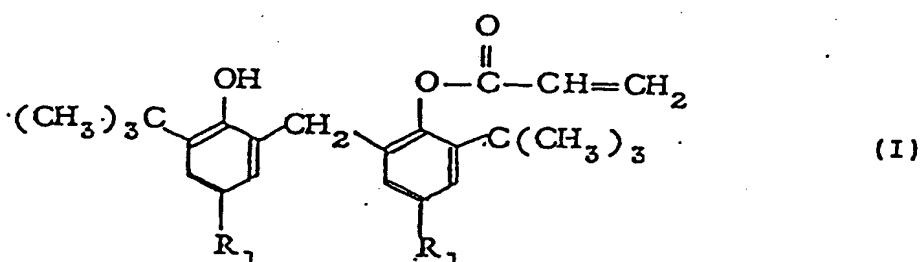


10 wherein the R_2 's and R_3 's are selected independently from a hydrogen atom and $\text{C}_1 - \text{C}_6$ alkyl groups and the R_4 's are the same or different $\text{C}_3 - \text{C}_{18}$ alkyl groups, the weight ratio of formula (I) compound to formula (II) compound being from 1:0.5 to 1:10 and the total amount of compounds (I) and (II) being 0.1 to 3 parts by weight based on 100 parts by weight of butadiene polymer.

- 15 2. A composition according to claim 1 wherein the weight ratio of formula (I) compound to formula (II) compound is 1:1 to 1:5
3. A composition according to claim 1 or 2 wherein the R_2 's and R_3 's are selected independently from a hydrogen atom and $\text{C}_1 - \text{C}_3$ alkyl groups and the R_4 's are the same or different $\text{C}_{12} - \text{C}_{18}$ alkyl groups.
- 20 4. A composition according to any preceding claim wherein R_1 is methyl or ethyl.
5. A composition according to any preceding claim wherein the total amount of compounds (I) and (II) is 0.2 to 2 parts by weight based on 100 parts by weight of butadiene polymer
- 25 6. A composition according to any preceding claim wherein the butadiene polymer comprises polymer selected from solution - polymerized polybutadiene rubber (BR); solution - polymerized styrene - butadiene copolymeric rubber (SBR), styrene - butadiene block copolymer (SBS); impact - resistant polystyrene modified with BR, SBR or SBS (HI - PS); and acrylonitrile - butadiene - styrene copolymer (ABS).

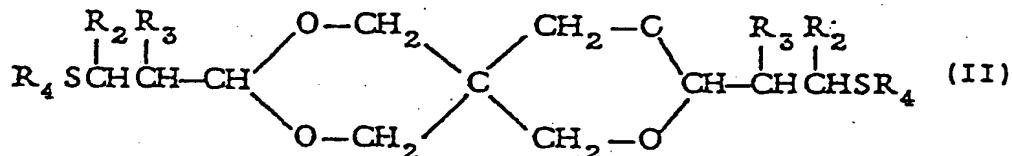
30 Patentansprüche

- 35 1. Butadienpolymer - Zusammensetzung, enthaltend mindestens eine Phenolverbindung (I)



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worin die Reste R_1 gleich oder verschieden voneinander $\text{C}_1 - \text{C}_4$ - Alkylreste sind, und mindestens eine Schwefel - enthaltende Verbindung (II).



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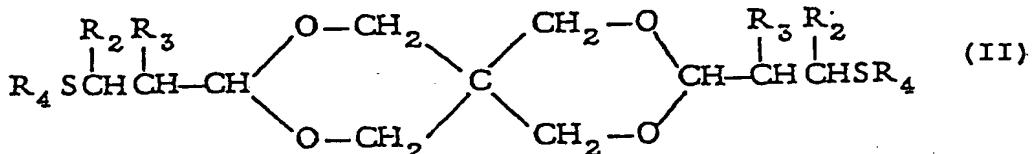
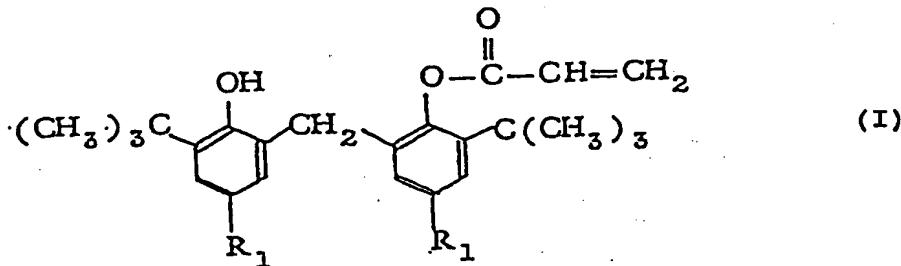
worin die Reste R_2 und R_3 unabhängig voneinander aus einem Wasserstoffatom und $\text{C}_1 - \text{C}_6$ - Alkylresten ausgewählt sind und die Reste R_4 gleich oder verschieden voneinander $\text{C}_3 - \text{C}_{18}$ -

Alkylreste sind, wobei das Gewichtsverhältnis der Formel (I) – Verbindung zur Formel (II) – Verbindung 1:0,5 bis 1:10 beträgt und die Gesamtmenge der Verbindungen (I) und (II) 0,1 bis 3 Gew. – Teile, basierend auf 100 Gew. – Teilen des Butadienpolymers, beträgt.

- 5 2. Zusammensetzung nach Anspruch 1, worin das Gewichtsverhältnis der Formel (I) – Verbindung zur Formel (II) – Verbindung 1:1 bis 1:5 beträgt.
3. Zusammensetzung nach Anspruch 1 oder 2, worin die Reste R_2 und R_3 unabhängig voneinander aus einem Wasserstoffatom und C_1 – C_3 – Alkylresten ausgewählt sind und die Reste R_4 gleich oder 10 verschieden voneinander C_{12} – C_{18} – Alkylreste sind.
4. Zusammensetzung nach einem der vorhergehenden Ansprüche, worin R_1 Methyl oder Ethyl ist.
5. Zusammensetzung nach einem der vorhergehenden Ansprüche, worin die Gesamtmenge der Verbindungen (I) und (II) 0,2 bis 2 Gew. – Teile, basierend auf 100 Gew. – Teilen des Butadienpolymers, beträgt.
6. Zusammensetzung nach einem der vorhergehenden Ansprüche, worin das Butadienpolymer ein aus Lösungs – polymerisiertem Polybutadiengummi (BR), Lösungs – polymerisiertem Styrol – Butadienco – 20 polymergummi (SBR), Styrol – Butadienblockcopolymer (SBS), schlagfestem, mit BR, SBR oder SBS (HI – PS) modifiziertem Polystyrol und Acrylonitril – Butadien – Styrolcopolymer (ABS) ausgewähltes Polymer umfaßt.

Revendications

- 25 1. Composition à base d'un polymère de butadiène contenant au moins un composé phénolique (I)



2. Composition suivant la revendication 1, dans laquelle le rapport en poids du composé de formule (I) au composé de formule (II) va de 1:1 à 1:5.

3. Composition suivant la revendication 1 ou 2, dans laquelle les groupes R_2 et R_3 sont choisis indépendamment entre un atome d'hydrogène et des groupes alkyle en C_1 à C_3 , et les groupes R_4 sont des groupes alkyle en C_{12} à C_{18} identiques ou différents.
- 5 4. Composition suivant l'une quelconque des revendications précédentes, dans laquelle R_1 est un groupe méthyle ou éthyle.
- 10 5. Composition suivant l'une quelconque des revendications précédentes, dans laquelle la quantité totale de composés (I) et (II) va de 0,2 à 2 parties en poids sur la base de 100 parties en poids de polymère de butadiène.
- 15 6. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le polymère de butadiène comprend un polymère choisi entre un caoutchouc de polybutadiène (BR) polymérisé en solution ; un caoutchouc copolymère de styrène – butadiène (SBR) polymérisé en solution ; un copolymère séquencé styrène – butadiène (SBS) ; un polystyrène résistant au choc modifié avec du BR, du SBR ou du SBS (HI-PS) ; et un copolymère acrylonitrile – butadiènestyrene (ABS).

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